Synthesis and molecular structure of $[(PPh_3)(C_6Cl_5)BrPt(\mu\text{-}Br)Ag(PPh_3)]_2$, a compound displaying strong and weak Ag...Br interactions

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Abstract

By reacting $(NBu_4)[trans\text{-}PtBr_2(C_6Cl_5)(PPh_3)]$ with $O_3ClOAgPPh_3$ the title compound has been obtained. Its structure has been established by single-crystal X-ray diffraction. The compound crystallizes in the monoclinic system, space group $P2_1/n$, with $a = 14.399(2)$, $b = 14.507(1)$, $c = 20.446(1)$ Å, $\beta = 94.81(1)°$, $V = 4256$ Å^3 and $Z = 4$. Residuals are $R = 0.040$ and $R_w = 0.041$. The '$PtBr_2(C_6Cl_5)PPh_3$' and '$AgPPh_3$' fragments are bonded by a single bromide bridge Pt(μ-Br)Ag (Pt–Br(1) = 2.434(1), Ag–Br(1) = 2.606(1) Å) and two $(PPh_3)(C_6Cl_5)BrPt(\mu\text{-}Br)Ag(PPh_3)$ molecules are connected through two weak Ag...Br interactions (Ag...Br = 3.109(2) Å). A short contact between one *o*-chlorine atom of the C_6Cl_5 group and the silver atom is also present (Ag...Cl(5) = 3.007(3) Å).

Introduction

During the last few years we have been engaged in the study of the reactions between anionic perhalophenyl-containing platinum(II) complexes and silver(I) salts or complexes and have found that these reactions lead to complexes with different stereochemical features depending on the C_6X_5 group (X = F, Cl) [1–4].

Very often, the heteronuclear Pt→Ag complexes have some of the C_6X_5 groups so positioned as to form *o*-X...Ag short contacts, implying donation of electron density from the X atom to the silver centre. Such weak interactions usually are stronger for the pentachloro than for the pentafluorophenyl derivatives [5], i.e. the values of the parameter ρ (= *o*-X...Ag exp distance/sum of the covalent radii $r_X + r_{Ag}$) [6] are greater for X = F than for X = Cl**, probably owing to the greater electronegativity of fluorine which makes it more reluctant to donate electron density. These weak interactions between already bonded halogens (for instance, in halocarbons) and other metal centres are noteworthy and infrequent, and only in very recent times has their study been a subject of growing interest [7–9].

For these reasons, an obvious extension of our work would be to prepare Pt→Ag complexes similar to those described above [1–4] but containing the pentabromophenyl group since the structural study of such complexes would allow us to compare the *o*-X...Ag contacts (X = F, Cl) with the *o*-Br...Ag ones. However unfortunately no pentabromophenyl platinum(II) complexes have been reported, i.e. the necessary precursors are lacking so far.

We have recently synthesized [4] the heteronuclear $(PPh_3)(C_6Cl_5)ClPt(\mu\text{-}Cl)Ag(PPh_3)$ complex whose crystal structure shows three different types of interactions between the silver centre and the coordinated chlorine atoms (see Fig. 1): (a) one chlorine atom acts as a bridge between the platinum and the silver atoms (Ag–Cl = 2.514 Å); (b) one *o*-Cl atom in the C_6Cl_5 ligand interacts with the Ag centre of the same unit (*o*-Cl...Ag = 3.041 Å) and (c) two binuclear Pt–Ag units are mutually linked through the Cl(bridging) atom on each unit (Ag...Cl′ = 3.023 Å) to form a tetranuclear cluster. The existence of such weak intermolecular Ag...Cl contacts (c) prompted us to prepare the similar bromide derivative $(PPh_3)(C_6Cl_5)BrPt(\mu\text{-}Br)Ag(PPh_3)$ and to study its structure in order to ascertain whether both complexes have similar structures and, in this case, to

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**For instance, the ρ values in the following complexes are: $(tht)(C_6F_5)_2(C_6Cl_5)PtAg(PPh_3)$, $\rho_F = 1.48$, 1.29; $\rho_{Cl} = 1.21$; $(NBu_4)[cis\text{-}(C_6F_5)_2(C_6Cl_5)_2PtAg(tht)]$, $\rho_F = 1.34$, 1.37; $\rho_{Cl} = 1.21$, 1.21 [5, 6].

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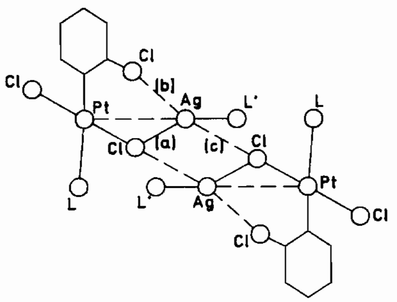

Fig. 1. Central core of the structure of $(PPh_3)(C_6Cl_5)ClPt(\mu$-$Cl)Ag(PPh_3)$ showing the three different types of Ag...Cl interactions.

obtain information about the role and structural influence of the halide ligands, with the Br...Ag weak interactions as our main point of interest.

Experimental

The C, H and N analyses were carried out with a Perkin-Elmer 240-B microanalyzer. IR spectra were recorded on a Perkin-Elmer 599 spectrophotometer (4000–200 cm^{-1}) using Nujol mulls between polyethylene sheets. Conductivities were measured in approximately 5×10^{-4} M acetone solutions with a Philips PW 9501/01 conductimeter. $(NBu_4)_2[Pt(\mu$-$Cl)Cl(C_6Cl_5)]_2$ was prepared as described elsewhere [10].

Preparation of $(NBu_4)_2[PtBr(\mu\text{-}Br)(C_6Cl_5)]_2$ *(1)*

0.2 g (0.132 mmol) of $(NBu_4)_2[PtCl(\mu$-$Cl)(C_6Cl_5)]_2$ and 0.069 g (0.79 mmol) of LiBr were refluxed for 12 h in acetone (20 ml). After evaporating to dryness, the residue was treated with 15 ml of dichloromethane to separate by filtration the LiCl formed and the excess of LiBr. The filtrate was evaporated to dryness and isopropyl alcohol was added to obtain **1** (90% yield). *Anal.* Calc. for $Pt_2Br_4Cl_{10}N_2C_{28}H_{72}$: C, 31.21; H, 4.25; N, 1.65. Found: C, 31.39; H, 4.20; N, 1.82%.

Preparation of $(NBu_4)[trans\text{-}PtBr_2(C_6Cl_5)(PPh_3)]$ *(2)*

To a solution of 0.25 g (0.148 mmol) of **1** in 25 ml of dichloromethane, 0.074 g (0.295 mmol) of PPh_3 was added. The mixture was reacted for 3 h at room temperature. After evaporating to dryness, isopropyl alcohol (5 ml) was added to the residue to render **2** as a light yellow solid. Yield 93%. *Anal.* Calc. for $PtBr_2Cl_5PNC_{40}H_{51}$: C, 43.32; H, 4.59; N, 1.26. Found: C, 43.27; H, 4.67; N, 1.31%.

Preparation of $(PPh_3)(C_6Cl_5)BrPt(\mu\text{-}Br)Ag(PPh_3)$ *(3)*

To a solution of 0.14 g (0.126 mmol) of **2** in 20 ml of dichloromethane, 0.059 g (0.1262 mmol) of $O_3ClOAgPPh_3$ was added. After 30 min stirring at room temperature, the solution was evaporated to dryness and isopropyl alcohol was added to obtain **3** as a yellow solid. Yield 80%. *Anal.* Calc. for $PtAgBr_2Cl_5P_2C_{42}H_{30}$: C, 40.84; H, 2.43. Found: C, 41.21; H, 2.77%.

Preparation of crystals for X-ray studies

Crystals of $(PPh_3)(C_6Cl_5)BrPt(\mu$-$Br)Ag(PPh_3)$ (**3**) were grown by slow diffusion of n-hexane into a solution of the complex in dichloromethane at −30 °C for *c.* 1 week.

X-ray structure analysis

A yellow crystal of complex **3** was mounted on a Siemens/STOE AED2 automated four circle diffractometer. Graphite monochromated Mo $K\alpha$ ($\lambda=0.71073$ cm^{-1}) radiation was used. A total of 6674 unique profile-fitted intensities [11] was collected using a ω–2θ scan technique at room temperature. No loss of intensity was observed during the data collection time. Data reduction included an absorption corrcction (10 ψ scans). Minimum and maximum transmission factors were 0.240 and 0.372.

The positions of the platinum and silver atoms were determined from the Patterson map. The remaining atoms were located in successive difference Fourier syntheses. Hydrogen atoms were not included. All atoms were refined with anisotropic temperature factors.

The final R factors are $R=0.0397$ and $R_w=0.0413$. The weighting scheme was $\omega^{-1}=\sigma^2(F)+0.000365F^2$. The Shelx program package was used in the determination of the structure [12].

Results and discussion

Synthesis of the complex $(PPh_3)(C_6Cl_5)BrPt(\mu\text{-}Br)Ag(PPh_3)$ *(3)*

Prior to the synthesis of the title complex the as yet unknown $(NBu_4)[PtBr_2(C_6Cl_5)(PPh_3)]$ (**2**) had to be prepared by halide exchange between LiBr (excess) and the chloride complex $(NBu_4)_2[PtCl(\mu$-$Cl)(C_6Cl_5)]_2$ and subsequent addition of the corresponding amount of PPh_3 (1:2 molar ratio) to the dichloromethane solutions. Both bromide complexes, the binuclear $(NBu_4)_2[PtBr(\mu$-$Br)(C_6Cl_5)]_2$ (**1**) and the mononuclear $(NBu_4)[PtBr_2(C_6Cl_5)(PPh_3)]$ (**2**) be-have in a similar way to the corresponding chloride derivatives [10].

By reacting at room temperature and in dichloromethane solution $(NBu_4)[PtBr_2(C_6Cl_5)(PPh_3)]$ (**2**) with $AgClO_4$ the neutral $(PPh_3)(C_6Cl_5)BrPt(\mu\text{-}Br)Ag(PPh_3)$ (**3**) can be isolated in good yield. (~80%). Analytical data (see 'Experimental') coincide with the proposed stoicheiometry. Acetone solutions of **3** are non-conducting, i.e. the donor solvent does not cleave the bonding interactions between the platinum- and silver-containing moieties. The IR spectrum of **3** shows the characteristic absorptions due to the C_6Cl_5 group (X-sensitive band at 863 cm^{-1} and ν(Pt–C) at 616 cm^{-1}) [13]; the absorptions due to PPh_3 appear at the usual values [4] while the ν(Pt–Br) vibration goes out of the lower limit of our apparatus (200 cm^{-1}).

Crystal structure of $(PPh_3)(C_6Cl_5)BrPt(\mu\text{-}Br)Ag(PPh_3)$

Crystal data collection details, fractional atomic coordinates and selected bond distances and angles are given in Tables 1, 2 and 3, respectively. The structure (Fig. 2) consists of two $(PPh_3)(C_6Cl_5)BrPt(\mu\text{-}Br)Ag(PPh_3)$ units connected by two Br(1)...Ag and Br(1')...Ag intermolecular interactions and re-

TABLE 1. Crystallographic data and data collection procedures for $(PPh_3)(C_6Cl_5)BrPt(\mu\text{-}Br)(PPh_3)$

Molecular formula	$PtAgBr_2Cl_5P_2C_{42}H_{30}$
Molecular weight	1235.07
Space group	monoclinic, $P2_1/n$
Crystal size (mm)	0.27×0.19×0.23
a (Å)	14.399(2)
b (Å)	14.507(1)
c (Å)	20.446(1)
β (°)	94.81(1)
V (Å³)	4256
Z	4
D_{calc} (g cm^{-3})	1.93
μ (cm^{-1})	58.24
Radiation	Mo Kα (λ=0.71073)
Diffractometer	Siemens/STOE AED2
Temperature (°C)	21±0.3
Scan technique	ω–2θ
2θ range (°)	4–50
Reflections measured	6939
Independent reflections	6674
Observed data with $F_o^2 > 3\sigma(F_o^2)$	4147
Refined parameters	477
R	0.040
R_w	0.041
Highest shift/e.s.d. (final cycle)	0.024
Highest residual peak (e Å^{-3})	1.1

TABLE 2. Fractional atomic coordinates (×10⁴) and isotropic equivalent thermal parameters and their e.s.d.s. for the complex $(PPh_3)(C_6Cl_5)BrPt(\mu\text{-}Br)Ag(PPh_3)$

	x	y	z	B (Å²)
Pt	4876(1)	3160(1)	3642(1)	8.34(6)
Ag	6061(1)	4101(1)	4660(1)	9.46(12)
Br1	4287(1)	4346(1)	4341(1)	10.41(16)
Br2	5319(1)	1832(1)	3035(1)	16.49(24)
P1	5330(2)	4184(2)	2845(1)	10.12(40)
P2	7694(2)	4373(2)	4872(1)	8.05(37)
Cl1	2731(2)	2487(3)	3522(2)	13.87(58)
Cl2	1825(3)	1040(3)	4356(2)	13.72(65)
Cl3	2970(3)	118(3)	5531(2)	16.99(80)
Cl4	5066(3)	611(2)	5833(2)	17.82(60)
Cl5	5982(2)	2085(2)	4993(2)	13.61(47)
C1	4333(7)	2221(7)	4257(5)	8.5(14)
C2	3411(8)	1975(7)	4142(5)	9.8(17)
C3	2975(8)	1336(8)	4525(7)	10.8(19)
C4	3480(10)	925(8)	5059(6)	9.9(20)
C5	4432(10)	1144(7)	5196(5)	12.0(19)
C6	4813(7)	1794(7)	4797(5)	9.6(15)
C7	4679(10)	3923(8)	2060(6)	13.2(19)
C8	5104(11)	4134(9)	1462(6)	21.6(25)
C9	4485(16)	3954(11)	869(7)	28.5(36)
C10	3600(18)	3668(11)	896(11)	20.3(36)
C11	3237(15)	3468(12)	1457(9)	18.6(37)
C12	3780(12)	3650(10)	2074(7)	14.3(28)
C13	5076(7)	5407(7)	2968(5)	9.9(15)
C14	5569(9)	5858(8)	3500(6)	11.6(20)
C15	5353(10)	6791(9)	3614(6)	11.5(21)
C16	4697(9)	7280(9)	3192(7)	13.0(20)
C17	4230(10)	6811(10)	2682(7)	17.4(24)
C18	4403(9)	5841(8)	2565(6)	14.3(19)
C19	6554(8)	4229(9)	2658(5)	11.0(19)
C20	7048(9)	3404(10)	2698(6)	14.3(21)
C21	7984(11)	3402(12)	2490(8)	16.7(28)
C22	8361(12)	4234(17)	2299(7)	22.8(37)
C23	7851(13)	5075(14)	2279(7)	15.8(34)
C24	6925(10)	5057(10)	2464(6)	13.9(24)
C25	8070(7)	5391(8)	4439(5)	8.1(15)
C26	7664(8)	6238(8)	4561(6)	11.0(19)
C27	7944(9)	7039(8)	4209(7)	11.1(19)
C28	8610(11)	6965(10)	3767(6)	12.9(27)
C29	9039(10)	6105(11)	3670(6)	12.0(20)
C30	8763(8)	5311(9)	3988(5)	11.9(14)
C31	8391(7)	3440(7)	4615(5)	7.8(19)
C32	7942(8)	2795(9)	4195(5)	13.7(13)
C33	8467(9)	2067(10)	3964(6)	13.6(23)
C34	9421(10)	1989(9)	4126(6)	14.8(22)
C35	9847(8)	2640(9)	4577(6)	13.7(20)
C36	9332(7)	3356(8)	4823(6)	10.7(16)
C37	8108(7)	4572(8)	5748(5)	11.3(16)
C38	7765(10)	3999(10)	6196(6)	15.5(25)
C39	8050(14)	4068(12)	6842(9)	18.6(35)
C40	8648(13)	4805(15)	7059(7)	28.3(36)
C41	8953(10)	5474(11)	6600(7)	17.4(27)
C42	8688(8)	5334(9)	5933(5)	10.6(20)

TABLE 3. Selected bond distances (Å) and angles (°) for the complex $(PPh_3)(C_6Cl_5)BrPt(\mu\text{-}Br)Ag(PPh_3)$

Bond distances			
Pt–Ag	2.918(1)	Pt–Br(1)	2.434(1)
Pt–Br(2)	2.406(1)	Pt–P(1)	2.338(3)
Pt–C(1)	2.053(10)	Ag–Br(1)	2.606(1)
Ag–P(2)	2.389(3)	Ag...Cl(5)	3.007(3)
Br(1)...Ag	3.109(1)	P(1)–C(7)	1.830(12)
P(1)–C(13)	1.832(10)	P(1)–C(19)	1.836(12)
P(2)–C(25)	1.827(11)	P(2)–C(31)	1.789(10)
P(2)–C(37)	1.863(10)	C(2)–Cl(1)	1.706(11)
C(3)–Cl(2)	1.718(13)	C(4)–Cl(3)	1.720(14)
C(5)–Cl(4)	1.711(11)	C(6)–Cl(5)	1.748(11)
Angles			
Br(1)–Pt–Ag	57.4(1)	Br(2)–Pt–Ag	125.3(1)
Br(2)–Pt–Br(1)	171.5(1)	P(1)–Pt–Ag	91.1(1)
P(1)–Pt–Br(1)	95.3(1)	P(1)–Pt–Br(2)	92.7(1)
C(1)–Pt–Ag	95.9(3)	C(1)–Pt–Br(1)	86.6(3)
C(1)–Pt–Br(2)	85.2(3)	C(1)–Pt–P(1)	172.6(3)
Br(1)–Ag–Pt	51.9(1)	P(2)–Ag–Pt	135.6(1)
P(2)–Ag–Br(1)	162.2(1)	Ag–Br(1)–Pt	70.6(1)

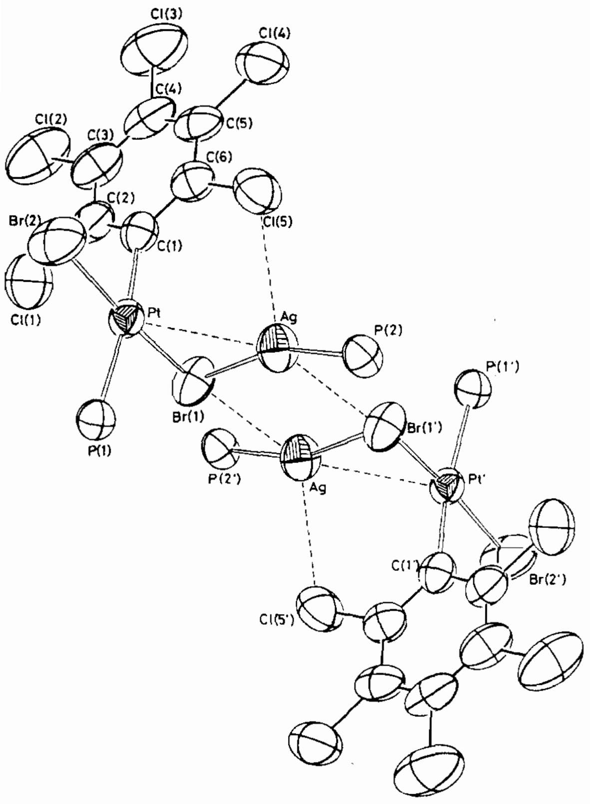

Fig. 2. ORTEP diagram of the crystal structure of $(PPh_3)(C_6Cl_5)BrPt(\mu\text{-}Br)Ag(PPh_3)$ showing the numbering scheme adopted. C_6H_5 rings of the PPh_3 groups have been omitted for clarity.

lated through a centre of symmetry. Each unit is formed by the '*trans*-$PtBr_2(C_6Cl_5)PPh_3$' and '$AgPPh_3$' moieties connected by a bromide bridge Pt(μ-Br)Ag(Pt–Br(1) = 2.434(1) Å, Ag–Br(1) = 2.606(1) Å).

The environment of the platinum atom is square planar with two *trans* Br(1) and Br(2) and the P (from PPh_3) and C_{ipso} (from C_6Cl_5) occupying the coordination sites, i.e., the same disposition as in the starting complex **2**. The Pt–Br(1) (bridge) distance (2.434(1) Å) is slightly longer than the Pt–Br(2) (terminal) one (2.406(1) Å). The Pt–C_{ipso} and Pt–P distances are within the usual ranges [4].

The silver atom is bonded to a PPh_3 group (Ag–P(2) = 2.389(3) Å) and to the bridging bromide ligand (Ag–Br(1) = 2.606(1) Å). Since the plane of the C_6Cl_5 group and the best least-squares plane containing the Pt atom form a dihedral angle of 86.22(5)°, one *o*-Cl atom is at 3.007(3) Å from the silver atom, thereby contributing to the stability and the structure of the binuclear complex. This is a new example of *o*-Cl...Ag interactions, other cases have previously been observed in binuclear platinum–silver complexes of different types [1, 4].

The Pt–Ag distance (2.918(1) Å) is longer than in other cases [4, 6] where a metal–metal bond has been invoked [1–3, 6], albeit this does not rule out some weak interaction. The Pt–Ag vector forms an angle of 33.65(5)° perpendicular to the platinum basal plane.

Finally, the whole structure is the result of another type of weak interaction since both $(PPh_3)(C_6Cl_5)$-$BrPt(\mu\text{-}Br)Ag(PPh_3)$ are connected by two Br(1)...Ag and Ag...Br(1')) intermolecular interactions.

Comparison of the structures of $(PPh_3)(C_6Cl_5)ClPt(\mu\text{-}Cl)Ag(PPh_3)$ and $(PPh_3)(C_6Cl_5)BrPt(\mu\text{-}Br)Ag(PPh_3)$

Both structures are very similar and the Pt–C(1), Pt–P(1) and Ag–P(2) distances coincide within experimental error, as can be seen from Table 4.

In order to compare the distances implying chloride or bromide atoms it seems appropriate to eliminate the effect of the greater size of the bromide ligand by using the parameter ρ (= Ag–X experimental distances/sum of covalent radii) [5] (values are given in Table 4).

The strength of the normal covalent bonds between Pt and Cl(1), Cl(2), Br(1) or Br(2) are practically the same ($\rho \sim 1.0$) while the bonds between Ag and Cl(1) or, respectively Br(1) are slightly weaker (ρ = 1.08, 1.05).

Concerning the weak interactions between the silver atom and the different types of halide ligands,

TABLE 4. Comparison of bond distances and ρ values for the complexes $(PPh_3)(C_6Cl_5)ClPt(\mu\text{-}Cl)Ag(PPh_3)$ and $(PPh_3)(C_6Cl_5)BrPt(\mu\text{-}Br)Ag(PPh_3)$

$(PPh_3)(C_6Cl_5)ClPt(\mu\text{-}Cl)Ag(PPh_3)$			$(PPh_3)(C_6Cl_5)BrPt(\mu\text{-}Br)Ag(PPh_3)$		
Pt–Ag	2.945(1)		Pt–Ag	2.918(1)	
Pt–C(1)	2.036(12)		Pt–C(1)	2.053(10)	
Pt–P(1)	2.334(3)		Pt–P(1)	2.338(3)	
Ag–P(2)	2.382(3)		Ag–P(2)	2.389(3)	
Pt–Cl(1)	2.341(3)	$\rho=1.02$	Pt–Br(1)	2.434(1)	$\rho=1.00$
Pt–Cl(2)	2.306(3)	$\rho=1.01$	Pt–Br(2)	2.406(1)	$\rho=0.99$
Ag–Cl(1)	2.514(2)	$\rho=1.08$	Ag–Br(1)	2.606(1)	$\rho=1.05$
Ag–Cl(7)	3.041(4)	$\rho=1.30$	Ag–Cl(5)	3.007(3)	$\rho=1.29$
Ag–Cl(1′)	3.023(2)	$\rho=1.30$	Ag–Br(1′)	3.109(2)	$\rho=1.25$

the *o*-Cl...Ag are of similar strength ($\rho=1.30$) in both complexes; however the intermolecular interaction Ag...X is slightly stronger for the bromo ($\rho=1.25$) than for the chloro compound ($\rho=1.30$). If it were only assignable to the different halide ligands it would document the greater availability of electron density drained from the less electronegative Br in comparison with the more electronegative Cl atom. Notwithstanding more significant differences between *o*-F...Ag and *o*-Cl...Ag ρ values have been observed in other complexes (see p.000).

Supplementary material

Anisotropic thermal parameters, observed and calculated structure factors and a full list of bond distances and angles are available from the authors upon request.

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